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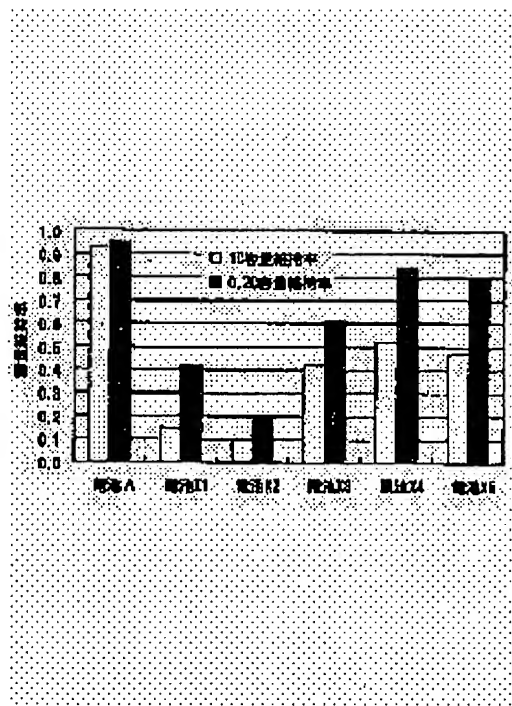
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## (54) NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive electrode active material for a non-aqueous electrolyte secondary battery having a high capacity maintaining rate and a good cyclic characteristic.

SOLUTION: A positive electrode active material of a non-aqueous electrolyte secondary battery is formed from a mixture of a first oxide consisting of spinel series oxide containing substantially lithium, manganese, and a metal other than manganese and oxygen, and a second oxide composed substantially of lithium, nickel, cobalt, a metal other than nickel and cobalt, and oxygen, being different from the first oxide.



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CLAIMS

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[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by using as a positive-electrode ingredient mixture which consists of a different metal from a lithium, manganese, a different metal from manganese, the first oxide that consists of spinel system oxide which consists of oxygen substantially, a lithium, nickel, cobalt, and nickel and cobalt, and the second oxide which consists of oxygen substantially and is different from said first oxide.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by for said first oxide being the oxide which replaced some manganese of a lithium-manganese multiple oxide by other elements, and said second oxide being the oxide which replaced some nickel of a lithium-nickel multiple oxide by cobalt and other elements.

[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 or 2 characterized by said first oxide being a lithium-manganese system multiple oxide expressed with empirical formula  $\text{LiXMn}_{2-y}\text{M}_1\text{yO}_{4+z}$  (M1 is at least one sort of elements chosen from the group which consists of aluminum, Co, nickel, Mg, and Fe, and is  $0 \leq x \leq 1.2$ ,  $0 < y \leq 0.1$ , and  $-0.2 \leq z \leq 0.2$ ).

[Claim 4] The nonaqueous electrolyte rechargeable battery according to claim 1 to 3 with which said second oxide is characterized by what is expressed with empirical formula  $\text{Li}_a\text{M}_2\text{b NicCodO}_2$  (M2 is at least one sort of elements chosen from the group which consists of aluminum, Mn, Mg, and Ti, and is  $0 < a < 1.3$ ,  $0.02 \leq b \leq 0.3$ ,  $0.02 \leq d/(c+d) \leq 0.9$ , and  $b+c+d=1$ ).

[Claim 5] Empirical formula  $\text{LiXMn}_{2-y}\text{M}_1\text{yO}_{4+z}$  of said first oxide Nonaqueous electrolyte rechargeable battery according to claim 3 which sets and is characterized by M1 being at least one sort of aluminum and Mg.

[Claim 6] Empirical formula  $\text{Li}_a\text{M}_2\text{b NicCodO}_2$  of said second oxide Nonaqueous electrolyte rechargeable battery according to claim 4 which sets and is characterized by M2 being Mn.

[Claim 7] Empirical formula  $\text{Li}_a\text{MnbNicCodO}_2$  of said second oxide Nonaqueous electrolyte rechargeable battery according to claim 6 which sets and is characterized by being  $0.1 \leq d/(c+d) \leq 0.5$ .

[Claim 8] The nonaqueous electrolyte rechargeable battery according to claim 1 to 7 characterized by mixing said first oxide and second oxide in said mixture by the weight ratios 20:80-80:20.

[Claim 9] The nonaqueous electrolyte rechargeable battery according to claim 1 to 8 characterized by the mean particle diameter of said first oxide being 5-30 micrometers.

[Claim 10] The nonaqueous electrolyte rechargeable battery according to claim 1 to 9 characterized by the mean particle diameter of said second oxide being 3-15 micrometers.

[Claim 11] A lithium, manganese, a different metal from manganese, and the first oxide that consists of a spinel system oxide which consists of oxygen substantially, A different metal from a lithium, nickel, cobalt, and nickel and cobalt, The second oxide which consists of oxygen substantially and is different from said first oxide, Consist of a lithium, cobalt, and oxygen or Or a lithium, The nonaqueous electrolyte rechargeable battery characterized by using as a positive-electrode ingredient mixture which consists of the third oxide which consists of cobalt, a different metal from cobalt, and oxygen, and is different from said first oxide and second oxide.

[Claim 12] The nonaqueous electrolyte rechargeable battery according to claim 11 characterized by for said first oxide being the oxide which replaced some manganese of a lithium-manganese multiple oxide by other elements, for said second oxide being the oxide which replaced some nickel of a lithium-nickel multiple oxide by cobalt and other elements, and said third oxide being the oxide which replaced some cobalt of a lithium-cobalt multiple oxide or this lithium-cobalt multiple oxide by other elements.

[Claim 13] The nonaqueous electrolyte rechargeable battery according to claim 11 or 12 characterized by said first oxide being a lithium-manganese system multiple oxide expressed with empirical formula  $\text{LiXMn}_{2-y}\text{M}_1\text{yO}_{4+z}$  ( $\text{M}_1$  is at least one sort of elements chosen from the group which consists of aluminum, Co, nickel, Mg, and Fe, and is  $0 \leq x \leq 1.2$ ,  $0 < y \leq 0.1$ , and  $-0.2 \leq z \leq 0.2$ ).

[Claim 14] The nonaqueous electrolyte rechargeable battery according to claim 11 to 13 with which said second oxide is characterized by what is expressed with empirical formula  $\text{Li}_a\text{M}_2\text{b NicCodO}_2$  ( $\text{M}_2$  is at least one sort of elements chosen from the group which consists of aluminum, Mn, Mg, and Ti, and is  $0 < a < 1.3$ ,  $0.02 \leq b \leq 0.3$ ,  $0.02 \leq d/(c+d) \leq 0.9$ , and  $b+c+d=1$ ).

[Claim 15] The nonaqueous electrolyte rechargeable battery according to claim 11 to 14 with which said third oxide is characterized by what is expressed with empirical formula  $\text{Li}_e\text{M}_3\text{fCo}_{1-f}\text{O}_2$  ( $\text{M}_3$  is at least one sort of elements chosen from the group which consists of aluminum, Mn, Mg, and Ti, and is  $0 < e < 1.3$  and  $0 \leq f \leq 0.4$ ).

[Claim 16] Empirical formula  $\text{LiXMn}_{2-y}\text{M}_1\text{yO}_{4+z}$  of said first oxide Nonaqueous electrolyte rechargeable battery according to claim 13 which sets and is characterized by  $\text{M}_1$  being at least one sort of aluminum and Mg.

[Claim 17] Empirical formula  $\text{Li}_a\text{M}_2\text{b NicCodO}_2$  of said second oxide Nonaqueous electrolyte rechargeable battery according to claim 14 which sets and is characterized by  $\text{M}_2$  being Mn.

[Claim 18] Empirical formula  $\text{Li}_a\text{MnbNicCodO}_2$  of said second oxide Nonaqueous electrolyte rechargeable battery according to claim 17 which sets and is characterized by being  $0.1 \leq d/(c+d) \leq 0.5$ .

[Claim 19] The nonaqueous electrolyte rechargeable battery according to claim 15 with which said third oxide is characterized by what is expressed with empirical formula  $\text{Li}_e\text{M}_3\text{fCo}_{1-f}\text{O}_2$  ( $\text{M}_3$  is Mg and at least one sort of elements chosen from the group which consists of Ti, and is  $0 < e < 1.3$  and  $0.02 \leq f \leq 0.2$ ).

[Claim 20] The nonaqueous electrolyte rechargeable battery according to claim 11 to 19 characterized by mixing said first oxide and second oxide in said mixture, and the third oxide by the weight ratio : (first oxide) (the second oxide + third oxide) = 20:80-80:20.

[Claim 21] The nonaqueous electrolyte rechargeable battery according to claim 20 characterized by mixing said second oxide and third oxide in said mixture by the weight ratio : (second oxide) (third oxide) = 90:10-10:90.

[Claim 22] The nonaqueous electrolyte rechargeable battery according to claim 11 to 21 characterized by the mean particle diameter of said first oxide being 5-30 micrometers.

[Claim 23] The nonaqueous electrolyte rechargeable battery according to claim 11 to 22 characterized by the mean particle diameter of said second oxide being 3-15 micrometers.

[Claim 24] The nonaqueous electrolyte rechargeable battery according to claim 11 to 23 characterized by the mean particle diameter of said third oxide being 3-15 micrometers.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to amelioration of the positive-electrode ingredient aiming at improvement in the load characteristic after a cycle in detail with respect to the nonaqueous electrolyte rechargeable battery represented by the lithium secondary battery.

[0002]

[Description of the Prior Art] In recent years, the nonaqueous electrolyte cell which uses a metal lithium or a lithium ion as a negative-electrode active material for occlusion, the alloy which may be emitted, or a carbon material, and uses a lithium-transition-metals multiple oxide as a positive-electrode ingredient attracts attention as a cell which has a high energy consistency.

[0003] If a lithium-cobalt multiple oxide ( $\text{LiCoO}_2$ ), a lithium-nickel multiple oxide ( $\text{LiNiO}_2$ ), a lithium-manganese multiple oxide ( $\text{LiMn}_2\text{O}_4$ ), etc. are used as positive active material into the multiple oxide of the above-mentioned lithium-transition metals, 4V class high discharge voltage will be obtained, and it becomes possible to raise especially the energy density of a cell.

[0004] By the way, promising \*\* of the lithium-manganese multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) which has Spinel structure is carried out from a viewpoint of the price of a raw material, and the supply stability of a raw material also in the multiple oxide used for an above-mentioned positive-electrode ingredient.

[0005] However, in using this lithium-manganese multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) for a positive-electrode ingredient, there is still room of amelioration. That is, this spinel type of multiple oxide is because the fall of the capacity accompanying advance of a charge-and-discharge cycle is large compared with the lithium-cobalt multiple oxide and lithium-nickel multiple oxide which do not have Spinel structure.

[0006] In order to solve this problem, it is reported by different-species elements', such as Co's, Cr's, and nickel's, permuting in part Mn atom of the lithium-manganese multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) which has Spinel structure, and strengthening the crystal structure from Mr. M. Wakihara etc., that a cycle property is improvable [refer to [ J. Electrochem. Soc. vol. 143, No. 1, and ] p178 (1996)].

[0007] However, even when such a permutation was performed, the improvement of a cycle property was not enough. The lithium-manganese system multiple oxide with which this reason has Spinel structure repeats expansion contraction at every charge and discharge of a rechargeable battery, and an active material particle also repeats expansion contraction in connection with this. for this reason, the reinforcement of a positive electrode -- falling -- contact of an active material particle and an electric conduction agent particle -- inadequate -- becoming -- that the utilization factor of a positive electrode falls \*\*\*\* -- or a positive electrode -- it is for the problem of a mixture exfoliating from a charge collector to occur.

[0008] then -- for example, the thing for which a lithium-manganese multiple oxide and a lithium-nickel system multiple oxide are mixed in JP,8-45498,A paying attention to contracting a lithium-nickel system multiple oxide conversely to a crystal expanding in case a lithium-manganese multiple oxide inserts a lithium ion -- a positive electrode -- a mixture -- controlling expansion and contraction on the whole is proposed.

[0009] moreover, the thing for which a lithium-cobalt multiple oxide mixes a lithium-nickel multiple oxide, a lithium-cobalt multiple oxide, and a lithium-nickel multiple oxide in JP,11-3698,A and JP,11-54122,A paying attention to having electronic conduction nature higher than a lithium-manganese multiple oxide -- a positive electrode -- a mixture -- raising the electronic conduction nature in the whole and raising a cycle property is proposed.

[0010]

[Problem(s) to be Solved by the Invention] However, even if it improves by above-mentioned mixing, there is room to improve a cycle property. Then, when this invention persons considered the fall of the capacity accompanying the cycle of the positive-electrode ingredient (active material) which mixed the lithium-manganese multiple oxide and lithium-nickel system multiple oxide which have Spinel structure, it turned out that the load characteristic is falling with progress of a cycle. That is, in order for a load characteristic to fall, when initial capacity and the capacity after a cycle were measured with a comparatively big current like 1C discharge, the capacity fall accompanying a cycle had occurred.

[0011] The purpose of this invention has a capacity maintenance factor in offering a high nonaqueous electrolyte rechargeable battery with a good cycle property.

[0012]

[Means for Solving the Problem] The nonaqueous electrolyte rechargeable battery according to the 1st aspect of affairs of this invention is characterized by to use as a positive-electrode ingredient mixture which consists of a different metal from a lithium, manganese, a different metal from manganese, the first oxide that consists of spinel system oxide which consists of oxygen substantially, a lithium, nickel, cobalt, and nickel and cobalt, and the second oxide which consists of oxygen substantially and is different from said first oxide.

[0013] Hereafter, the 1st aspect of affairs of this invention is explained. Specifically as the first oxide, the oxide which replaced some manganese of a lithium-manganese multiple oxide by other elements is mentioned. Specifically as the second oxide, the oxide which replaced some nickel of a lithium-nickel multiple oxide by cobalt and other elements is mentioned.

[0014] The fall of the load characteristic accompanying progress of a cycle can be controlled by using the first oxide which replaced some manganese of the lithium-manganese multiple oxide which has Spinel structure by other elements, and the second oxide which replaced some nickel of a lithium-nickel multiple oxide by cobalt and other elements. As this 1st reason, by making a different-species element dissolve, respectively, the electronic state of the active material of the first oxide and the second oxide changes, and since the electronic conduction nature of the whole active material improved, it thinks. Moreover, as the 2nd reason, since the lithium-manganese system multiple oxide to which a crystal expands by insertion of a lithium ion, and the lithium-nickel-cobalt system multiple oxide which a crystal contracts by insertion of a lithium ion are used, it thinks because contact between the particles of the first oxide accompanying progress of a cycle and the second oxide is maintained by stability.

[0015] Here, the lithium-manganese system multiple oxide expressed with empirical formula  $\text{LiXMn}_{2-y}\text{M}_1\text{yO}_{4+z}$  ( $\text{M}_1$  is at least one sort of elements chosen from the group which consists of aluminum, Co, nickel, Mg, and Fe, and is  $0 \leq x \leq 1.2$ ,  $0 < y \leq 0.1$ , and  $-0.2 \leq z \leq 0.2$ ) which has Spinel structure as said first oxide can be illustrated. And it is empirical formula  $\text{LiXMn}_{2-y}\text{M}_1\text{yO}_{4+z}$  also in this. As  $\text{M}_1$  which can be set, at least one sort of aluminum and Mg is suitable.

[0016] On the other hand, as said second oxide, the multiple oxide expressed with empirical formula  $\text{Li}_a\text{M}_{2b}\text{Ni}_c\text{Co}_d\text{O}_2$  ( $\text{M}_2$  is at least one sort of elements chosen from the group which consists of aluminum, Mn, Mg, and Ti, and is  $0 < a < 1.3$ ,  $0.02 \leq b \leq 0.3$ ,  $0.02 \leq d/(c+d) \leq 0.9$ , and  $b+c+d=1$ ) can be illustrated. And  $\text{M}_2$  is set to Mn also in this, and it is an empirical formula  $\text{Li}_a\text{Mn}_b\text{Ni}_c\text{Co}_d\text{O}_2$ . The second oxide which sets and is set to  $0.1 \leq d/(c+d) \leq 0.5$  is the optimal.

[0017] And in said mixture, it is optimal that said first oxide and second oxide set to 20:80-80:20 by the weight ratio from a viewpoint that high capacity is maintainable. Since the whole electronic conduction nature improves more and contact of the particle comrade of the first oxide and the second oxide is maintained more by stability when it is in this range, the fall of the load characteristic accompanying progress of a cycle is controlled.

[0018] Moreover, as for the mean diameter of the lithium-nickel-cobalt system multiple oxide whose mean diameters of the lithium-manganese system multiple oxide which is the first oxide of the above are 5-30 micrometers and the second oxide of the above, it is desirable that it is 3-15 micrometers, and such combination is the most desirable. In addition, the one where the particle size of the first oxide is larger than the particle size of the second oxide is desirable. the case where particle size is in the above-mentioned range -- contact of the particle comrade of each multiple oxide -- more -- increasing -- a mixture -- since the whole electronic conduction nature improves, and since expansion contraction of each multiple oxide is offset more effectively and contact of the particle comrade of each multiple oxide is maintained more by stability, the fall of the load characteristic accompanying progress of a cycle is controlled. here -- mean particle diameter -- positive active material or a positive electrode -- the mixture was observed with the scanning electron microscope (SEM), the magnitude of the longitudinal direction of five particles in the active material particle contained for 100 micrometer around was measured, and it asked as an average of the magnitude of all particles. By each above-mentioned configuration, a nonaqueous electrolyte rechargeable battery with the high dependability to which a load characteristic does not fall by progress of a charge-and-discharge cycle, either can be offered.

[0019] The nonaqueous electrolyte rechargeable battery according to the 2nd aspect of affairs of this invention A lithium, manganese, a different metal from manganese, and the first oxide that consists of a spinel system oxide which consists of oxygen substantially, A different metal from a lithium, nickel, cobalt, and nickel and cobalt, The second oxide which consists of oxygen substantially and is different from said first oxide, It consists of a metal which consists of a lithium, cobalt, and oxygen or is different from a lithium, cobalt, and cobalt, and oxygen, and is characterized by using as a positive-electrode ingredient mixture which consists of the third different oxide from said first oxide and second oxide.

[0020] Hereafter, the 2nd aspect of affairs of this invention is explained. As the first oxide and the second oxide, the 1st first oxide and second oxide in an aspect of affairs of this invention can be used.

[0021] Specifically as the third oxide, the oxide which replaced some cobalt of a lithium-cobalt multiple oxide or this lithium-cobalt multiple oxide by other elements is mentioned.

[0022] Also in the 2nd aspect of affairs, since the 1st first same oxide and second same oxide as an aspect of affairs are used, the fall of the load characteristic accompanying progress of a cycle can be controlled for the same reason as the 1st aspect of affairs.

[0023] In the 2nd aspect of affairs, the third oxide is further mixed and used for the first oxide and the second oxide. [M.Menetrier et al which can prevent the fall of the load characteristic accompanying a cycle further since the electronic conduction nature of the third oxide is higher than the electronic conduction nature of the first oxide and the second oxide -- " -- The Second Japan-France Joint Seminar on LithiumBatteries and November 23 - 24, 1998, Morioka, Japan", and p.83 reference].

[0024] As said third oxide, the multiple oxide expressed with empirical formula  $\text{Li}e\text{M}_3\text{fCo}_1\text{-fO}_2$  ( $\text{M}_3$  is at least one sort of elements chosen from the group which consists of aluminum, Mn, Mg, and Ti, and is  $0 < e < 1.3$  and  $0 \leq f \leq 0.4$ ) can be illustrated. And  $\text{M}_3$  is made into at least one sort of Mg and Ti also in this, and it is empirical formula  $\text{Li}e\text{M}_3\text{fCo}_1\text{-fO}_2$ . The third oxide which sets and is set to  $0.02 \leq f \leq 0.2$  is suitable.

[0025] And in said mixture, it is suitable to set said first oxide, second oxide, and third oxide to : (first oxide) (the second oxide + third oxide) = 20:80-80:20 by the weight ratio from a viewpoint that high capacity is maintainable. Since the whole electronic conduction nature improves more and contact of the particle comrade of the first oxide, the second oxide, and the third oxide is maintained more by stability when it is in this range, the fall of the load characteristic accompanying progress of a cycle is controlled.

[0026] It is optimal to set said second oxide and third oxide in said mixture to : (second oxide) (third oxide) = 90:10-10:90 by the weight ratio furthermore from a viewpoint that high capacity is maintainable. When it is in this range, the whole electronic conduction nature improves further and the fall of the load characteristic accompanying progress of a cycle is controlled further.

[0027] Moreover, as for the mean diameter of the lithium-cobalt system multiple oxide whose mean diameters of the lithium-nickel-cobalt system multiple oxide whose mean diameters of the lithium-



manganese system multiple oxide which is the first oxide of the above are 5-30 micrometers and the second oxide of the above are 3-15 micrometers and the third oxide of the above, it is desirable that it is 3-15 micrometers, and such combination is the most desirable. In addition, the one where the particle size of the first oxide is larger than the particle size of the second oxide and the third oxide is desirable. the case where particle size is in the above-mentioned range -- contact of the particle comrade of each multiple oxide -- more -- increasing -- a mixture -- since the whole electronic conduction nature improves, and since expansion contraction of each multiple oxide is offset more effectively and contact of the particle comrade of each multiple oxide is maintained more by stability, the fall of the load characteristic accompanying progress of a cycle is controlled. It can ask for mean particle diameter like the 1st aspect of affairs of this invention here.

[0028] By each above-mentioned configuration, a nonaqueous electrolyte rechargeable battery with the high dependability to which a load characteristic does not fall by progress of a charge-and-discharge cycle, either can be offered. Hereafter, the matter common to the 1st aspect of affairs and 2nd aspect of affairs of this invention is explained as "this invention."

[0029] About other cell ingredients other than the positive-electrode ingredient used for this invention, a well-known ingredient can be conventionally used especially without a limit as an object for nonaqueous electrolyte rechargeable batteries. and carbon materials, such as lithium alloys, such as a lithium-aluminium alloy which is a lithium metal or the matter which can occlusion emit a lithium as a negative-electrode ingredient, a lithium-lead alloy, and a lithium-tin alloy, a graphite, corks, and an organic substance baking object, SnO<sub>2</sub>, SnO and TiO<sub>2</sub>, and Nb<sub>2</sub>O<sub>3</sub> etc. -- compared with positive active material, a less noble metal oxide is illustrated for potential.

[0030] Moreover, as a solvent of nonaqueous electrolyte, a mixed solvent with low-boiling point solvents, such as high-boiling point solvents, such as ethylene carbonate (EC), propylene carbonate (PC), vinylene carbonate (VC), and butylene carbonate (BC), these and dimethyl carbonate (DMC), diethylene carbonate (DEC), methylethyl carbonate (EMC), 1, 2-diethoxy ethane (DEE), 1, 2-dimethoxyethane (DME), and ethoxy methoxyethane (EME), is illustrated.

[0031]

[Embodiment of the Invention] It is possible to change this invention suitably in the range which is not limited at all by the following example and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

[0032] The following experiments 1 - experiment 3 show the example according to the 1st aspect of affairs of this invention.

<Experiment 1> In this experiment 1, the class of positive-electrode ingredient was replaced with, the cell was produced, and that property was compared.

[0033] (Example) Production of a positive electrode is described first. A lithium hydroxide (LiOH), a manganese sulfate (Mn<sub>2</sub> (NO<sub>3</sub>)), and an aluminium nitrate (aluminum<sub>3</sub> (NO<sub>3</sub>)) are ground after 20-hour heat treatment at 800 degrees C in atmospheric air, after aluminum is mixed so that Li and Mn may serve as a mole ratio of 1:1.95:0.05, and it is empirical formula LiMn<sub>1.95</sub>aluminum<sub>0.05</sub>O<sub>4</sub> of 15 micrometers of mean diameters. The lithium-manganese system multiple oxide (the first oxide) expressed was obtained. This first oxide has Spinel structure.

[0034] Moreover, LiOH, nickel nitrate (nickel<sub>2</sub> (NO<sub>3</sub>)), a cobalt nitrate (Co<sub>2</sub> (NO<sub>3</sub>)), and manganese nitrate (Mn<sub>2</sub> (NO<sub>3</sub>)) After mixing so that Li, nickel, and Co and Mn may serve as a mole ratio of 1:0.6:0.3:0.1, It grinds after 20-hour heat treatment at 750 degrees C in an oxygen ambient atmosphere, and is empirical formula LiNi<sub>0.6</sub>Co<sub>0.3</sub>Mn<sub>0.1</sub>O<sub>2</sub> of 10 micrometers of mean diameters. The lithium-nickel-cobalt system multiple oxide (the second oxide) expressed was obtained.

[0035] Thus, it mixed so that it might be set to 1:1 by the weight ratio, and the first oxide and the second oxide which were obtained were used as the positive-electrode ingredient (positive active material). The powder 90 weight section of this positive active material, the artificial-graphite powder 5 weight section, and the N-methyl-2-pyrrolidone (NMP) solution of the polyvinylidene fluoride 5 weight section were mixed, and the slurry was adjusted. After applying this slurry to both sides of aluminium foil with the doctor blade method and forming an active material layer, the vacuum drying was carried out at 150



degrees C for 2 hours, and the positive electrode was produced.

[0036] Next, the natural-graphite 95 weight section and the NMP solution of the polyvinylidene fluoride 5 weight section were mixed, and the carbon slurry was adjusted. After applying this carbon slurry to both sides of copper foil with the doctor blade method and forming a carbon layer, the vacuum drying was carried out at 150 degrees C for 2 hours, and the negative electrode was produced.

[0037] And as nonaqueous electrolyte, it is one mol [l. ] LiPF<sub>6</sub> to the mixed solvent of the volume ratio 1:1 of ethylene carbonate and dimethyl carbonate. What was melted and prepared was used.

[0038] this invention cell A of the nonaqueous electrolyte rechargeable battery (cell dimension:; with a diameter of 14mm height of 50mm, nominal capacity 580mAh) of AA size was produced using a positive electrode, an above-mentioned negative electrode, and an above-mentioned nonaqueous electrolyte. In addition, the fine porosity film made from polypropylene is used as a separator.

[0039] (Example 1 of a comparison) In the positive electrode of the above-mentioned example, the comparison cell X1 as well as the above-mentioned this invention cell A was produced except using only a lithium-manganese system multiple oxide (the first oxide) as positive active material.

[0040] (Example 2 of a comparison) It sets to the positive electrode of the above-mentioned example, and is LiMn<sub>2</sub>O<sub>4</sub> as positive active material. The comparison cell X2 as well as the above-mentioned this invention cell A was produced except using only the lithium-manganese multiple oxide (spinel manganese) expressed.

[0041] (Example 3 of a comparison) In the positive electrode of the above-mentioned example, the comparison cell X3 as well as the above-mentioned this invention cell A was produced except having used only the lithium-nickel-cobalt system multiple oxide (the second oxide) as positive active material.

[0042] (Example 4 of a comparison) It sets to the positive electrode of the above-mentioned example, and is an empirical formula LiMn<sub>2</sub>O<sub>4</sub> as the first oxide. The comparison cell X4 was produced like the example 1 except using the lithium-manganese multiple oxide (spinel manganese) expressed.

[0043] (Example 5 of a comparison) In the positive electrode of the above-mentioned example, the comparison cell X5 as well as the above-mentioned this invention cell A was produced except using the lithium-nickel-cobalt system multiple oxide expressed with empirical formula LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> as the second oxide.

[0044] The positive-electrode ingredient of the produced cell is shown in Table 1 as above-mentioned.

[0045]

[Table 1]

電池種	正極材料
本發明電池A	LiMn <sub>1.55</sub> Al <sub>0.55</sub> O <sub>4</sub> LiNi <sub>0.8</sub> Co <sub>0.2</sub> Mn <sub>0.1</sub> O <sub>2</sub>
比較電池X1	LiMn <sub>1.55</sub> Al <sub>0.55</sub> O <sub>4</sub>
比較電池X2	LiMn <sub>2</sub> O <sub>4</sub>
比較電池X3	LiNi <sub>0.8</sub> Co <sub>0.2</sub> Mn <sub>0.1</sub> O <sub>2</sub>
比較電池X4	LiMn <sub>2</sub> O <sub>4</sub> LiNi <sub>0.8</sub> Co <sub>0.2</sub> Mn <sub>0.1</sub> O <sub>2</sub>
比較電池X5	LiMn <sub>1.55</sub> Al <sub>0.55</sub> O <sub>4</sub> LiNi <sub>0.8</sub> Co <sub>0.2</sub> O <sub>2</sub>

[0046] (Charge and discharge test) After carrying out constant-current charge of each cell of this invention cell A produced as mentioned above next and reference electrodes X1-X5 to 4.2V by 580mA which is the current value which is equivalent to 1C at a room temperature (25 degrees C), respectively,

constant-current discharge was carried out to 2.75V by 580mA which is the current value which performs 4.2V constant-potential charge with 50mA of termination currents further, and is equivalent to 1C after that. It is the 1C capacity A1 about the discharge capacity at this time. It carried out.

[0047] Subsequently, constant current is performed to 2.75V by 116mA which is a current value equivalent to 0.2C after performing the same charge as the above, and it is the 0.2C capacity B1 about the discharge capacity at this time. It carried out.

[0048] Next, 200 cycle charge and discharge were performed by having made the charge and discharge at the time of measuring 1C capacity into 1 cycle, the same measurement as the above was performed after that, and the 1C capacity A200 and the 0.2C capacity B200 were calculated. And 1C capacity maintenance factors A200/A1 after 200 cycles and the 0.2C capacity maintenance factors B200/B1 It asked.

[0049] This result is shown in drawing 1. In addition, it is shown that the load characteristic is falling by the cycle, so that the difference of 1C capacity maintenance factor and a 0.2C capacity maintenance factor is large to this result.

[0050] By making a different-species element (aluminum) dissolve from contrast of the comparison cell X1 and the comparison cell X2 to the lithium-manganese multiple oxide (LiMn 2O4) which is the first oxide shows that 1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved. This is because the crystal structure was strengthened and degradation of the crystal structure accompanying charge and discharge was controlled by making a different-species element dissolve to the first oxide.

[0051] Moreover, it sets to a positive electrode from contrast with the comparison cell X3 - the comparison cell X5, and the comparison cell X1 and the comparison cell X2. LiMn 2O4 LiNi0.6Co0.3Mn 0.1O2 LiNi0.8Co 0.2O2 Moreover, LiMn1.95aluminum 0.05O4 By mixing LiNi0.8Co 0.2O2 It turns out that 1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved rather than the case where it is independent respectively. the mixture accompanying [ when this mixes a lithium-manganese system multiple oxide and a lithium-nickel-cobalt system multiple oxide ] charge and discharge -- it is because the whole expansion contraction was controlled.

[0052] Moreover, the comparison of this invention cell A and the comparison cells X3-X5 to LiMn1.95aluminum 0.05O4 LiNi0.6Co0.3Mn 0.1O2 1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved greatly, and the difference of 1C capacity maintenance factor and a 0.2C capacity maintenance factor decreases greatly, and by mixing shows that the fall of the load characteristic accompanying a cycle can be controlled. Since the electronic state of the active material which consists of the second oxide changed for a start and the whole electronic conduction nature improved by making a different-species element dissolve to a lithium-manganese system multiple oxide and each lithium-nickel-cobalt system multiple oxide, and since the expansion contraction behavior accompanying those charges and discharges changed and contact of the particle comrade of the first oxide accompanying the progress which is a cycle, and the second oxide was maintained by stability, this is considered.

[0053] It is empirical formula LiMn1.95aluminum 0.05O4 as the first oxide which made the different-species element dissolve in the above-mentioned example. Although the oxide was used empirical formula  $\text{LiXMn}_2\text{-yM}_1\text{yO}_4\text{+z}$  (M1 -- aluminum, Co, and nickel --) When the lithium-manganese system multiple oxide which are at least one sort of elements chosen from the group which consists of Mg and Fe, and is expressed with  $0 \leq x \leq 1.2$ ,  $0 < y \leq 0.1$ , and  $-0.2 \leq z \leq 0.2$  is used, it is checking that the same effectiveness is acquired.

[0054] Moreover, although the thing of empirical formula LiNi0.6Co0.3Mn 0.1O2 was used in the above-mentioned example on the other hand as a lithium-nickel-cobalt system multiple oxide (the second oxide) which made the different-species element dissolve Li<sub>a</sub>M<sub>2b</sub>Ni<sub>c</sub>O<sub>d</sub>2 (M2 is at least one sort of elements chosen from the group which consists of aluminum, Mn, Mg, and Ti) And when the lithium-nickel-cobalt system multiple oxide expressed with  $0 < a < 1.3$ ,  $0.02 \leq b \leq 0.3$ ,  $0.02 \leq d/(c+d) \leq 0.9$ , and  $b+c+d=1$  is used, it is checking that the same effectiveness is acquired.

[0055] <Experiment 2> In this experiment 2, addition of the first oxide in a positive-electrode ingredient

and the second oxide and a content ratio were changed, and the property of a cell was compared.

[0056] this invention cell A of an example -- setting -- the weight of the first oxide and the second oxide -- a cell B1 - B4 were produced like the example except changing a mixing ratio with 10:90, 20:80, 80:20, and 90:10. And 1C capacity maintenance factor and the 0.2C capacity maintenance factor were measured like the case of the above-mentioned experiment 1. The result is shown in drawing 2.

[0057] In this drawing 2, the result of the cell A (weight of the first oxide: weight =50:50 of the second oxide) used in the above-mentioned experiment 1 is also written together. The result of drawing 2 shows that 1C capacity maintenance factor and a 0.2C capacity maintenance factor improve, and the fall of the load characteristic accompanying a cycle can be controlled, when the mixing ratio of the lithium-manganese system multiple oxide in the above-mentioned mixture, i.e., the first oxide, is 20 - 80 % of the weight. This is considered to be because for contact of the particle comrade of the first oxide accompanying progress of a cycle and the lithium-nickel-cobalt system multiple oxide which is the second oxide to have been more maintainable to stability when the mixing ratio of the first oxide is in the above-mentioned range.

[0058] <Experiment 3> In this experiment 3, the mean particle diameter of the first oxide in a positive-electrode ingredient and the second oxide was changed, and the property of a cell was compared.

[0059] In the above-mentioned this invention cell A, the cell C1 - the cell C8 were produced like the above-mentioned example except obtaining the positive-electrode ingredient which has the particle size shown in Table 2 by controlling the grinding process at the time of compounding the first oxide and the second oxide.

[0060]

[Table 2]

	第一酸化物の粒径	第二酸化物の粒径
電池 C 1	1 5 $\mu$ m	2 $\mu$ m
電池 C 2	1 5 $\mu$ m	3 $\mu$ m
電池 A	1 5 $\mu$ m	1 0 $\mu$ m
電池 C 3	1 5 $\mu$ m	1 5 $\mu$ m
電池 C 4	1 5 $\mu$ m	2 0 $\mu$ m
電池 C 5	3 $\mu$ m	1 0 $\mu$ m
電池 C 6	5 $\mu$ m	1 0 $\mu$ m
電池 C 7	3 0 $\mu$ m	1 0 $\mu$ m
電池 C 8	3 5 $\mu$ m	1 0 $\mu$ m

[0061] And 1C capacity maintenance factor and the 0.2C capacity maintenance factor were measured like the case of the above-mentioned experiment 1 using the above-mentioned cells C1-C8. The result is shown in drawing 3. The data of this invention cell A prepared in the experiment 1 mentioned above are also collectively shown in this table.

[0062] When it is in the range whose mean diameter of the first oxide which consists of a lithium-manganese system multiple oxide is 5-30 micrometers, and the range whose mean diameter of the second oxide which is a lithium-nickel-cobalt system multiple oxide is 3-15 micrometers from the result of drawing 3, it turns out that 1C capacity maintenance factor and a 0.2C capacity maintenance factor improve, and the fall of the load characteristic accompanying a cycle can be controlled especially.

[0063] the case where especially the mean particle diameter of each multiple oxide is contained in the above-mentioned range -- contact of the particle comrade of each multiple oxide -- more -- increasing -- a positive electrode -- a mixture -- since the whole electronic conduction nature improves, and since expansion contraction of each multiple oxide is offset more effectively, the property of cells C2, A, C3, C6, and C7 is considered to be good. Moreover, the comparison of cells C2, A, and C7 and cells C3 and

C6 shows that the one where the particle size of the first oxide is larger than the particle size of the second oxide is desirable.

[0064] The following experiments 4 - experiment 7 show the example according to the 2nd aspect of affairs of this invention.

<Experiment 4> In this experiment 4, the class of positive-electrode ingredient was replaced with, the cell was produced, and that property was compared.

[0065] (Example) The first oxide and the second oxide were obtained like the above-mentioned experiment 1. After mixing LiOH, a cobalt nitrate ( $\text{Co}_2(\text{NO}_3)_3$ ), and a magnesium nitrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) about the third oxide so that Li, and Co and Mg may serve as a mole ratio of 1:0.9:0.1, it grinds after 20-hour heat treatment at 750 degrees C in dry air, and it is  $\text{LiCo}_{0.9}\text{Mg}_{0.1}\text{O}_2$  of 10 micrometers of mean diameters. The lithium-cobalt system multiple oxide (the third oxide) expressed was obtained.

[0066] Thus, it mixed so that it might be set to 1:0.5:0.5 by the weight ratio, and the first oxide, the second oxide, and the third oxide which were obtained were used as the positive-electrode ingredient (positive active material). The positive electrode was produced like the above-mentioned experiment 1 using this positive active material.

[0067] A negative electrode and nonaqueous electrolyte were produced like the above-mentioned experiment 1. this invention cell D was produced like the above-mentioned experiment 1 using the positive electrode, the negative electrode, and nonaqueous electrolyte which were obtained.

[0068] (Example 6 of a comparison) In the positive electrode of the above-mentioned example, the comparison cell Y1 as well as the above-mentioned this invention cell D was produced except using what mixed the lithium-manganese system multiple oxide (the first oxide) and the lithium-cobalt system multiple oxide (the third oxide) as positive active material so that it might be set to 1:1 by the weight ratio.

[0069] (Example 7 of a comparison) In the positive electrode of the above-mentioned example, the comparison cell Y2 as well as the above-mentioned this invention cell D was produced except using only a lithium-manganese system multiple oxide (the first oxide) as positive active material.

[0070] (Example 8 of a comparison) It sets to the positive electrode of the above-mentioned example, and is  $\text{LiMn}_2\text{O}_4$  as positive active material. The comparison cell Y3 as well as the above-mentioned this invention cell D was produced except using only the lithium-manganese multiple oxide (spinel manganese) expressed.

[0071] (Example 9 of a comparison) In the positive electrode of the above-mentioned example, the comparison cell Y4 as well as the above-mentioned this invention cell D was produced except having used only the lithium-nickel-cobalt system multiple oxide (the second oxide) as positive active material.

[0072] (Example 10 of a comparison) In the positive electrode of the above-mentioned example, the comparison cell Y5 as well as the above-mentioned this invention cell D was produced except having used only the lithium-cobalt system multiple oxide (the third oxide) as positive active material.

[0073] (Example 11 of a comparison) It sets to the positive electrode of the above-mentioned example, and is an empirical formula  $\text{LiMn}_2\text{O}_4$  as the first oxide. The lithium-manganese multiple oxide (spinel manganese) expressed is used. The comparison cell Y6 as well as the above-mentioned this invention cell D was produced except using what mixed the lithium-manganese multiple oxide (the first oxide) and the lithium-nickel-cobalt system multiple oxide (the second oxide) so that it might be set to 1:1 by the weight ratio.

[0074] In the positive electrode of the above-mentioned example, the lithium-nickel-cobalt system multiple oxide expressed with empirical formula  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  as the second oxide is used.

(Example 12 of a comparison) The comparison cell Y7 as well as the above-mentioned this invention cell D was produced except using what mixed the lithium-manganese system multiple oxide (the first oxide) and the lithium-nickel-cobalt system multiple oxide (the second oxide) so that it might be set to 1:1 by the weight ratio.

[0075] (Example 13 of a comparison) It sets to the positive electrode of the above-mentioned example, and is an empirical formula  $\text{LiMn}_2\text{O}_4$  as the first oxide. The comparison cell Y8 as well as the above-mentioned this invention cell D was produced except using the lithium-manganese multiple oxide

(spinel manganese) expressed.

[0076] (Example 14 of a comparison) In the positive electrode of the above-mentioned example, the comparison cell Y9 as well as the above-mentioned this invention cell D was produced except using the lithium-nickel-cobalt system multiple oxide expressed with empirical formula  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  as the second oxide.

[0077] In addition, the comparison cells Y2, Y3, Y4, Y6, and Y7 are the respectively same cells as the comparison cells X1, X2, X3, X4, and X5 in experiment 1. The positive-electrode ingredient of the cell produced as above-mentioned is shown in Table 3. In addition, in Table 3, this invention cell A in the above-mentioned experiment 1 is shown collectively.

[0078]

[Table 3]

電池種	正極材料
本發明電池D	$\text{LiMn}_{1.95}\text{Al}_{0.05}\text{O}_4$ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ $\text{LiCo}_{0.8}\text{Mg}_{0.1}\text{O}_2$
本發明電池A	$\text{LiMn}_{1.95}\text{Al}_{0.05}\text{O}_4$ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$
比較電池Y1	$\text{LiMn}_{1.95}\text{Al}_{0.05}\text{O}_4$ $\text{LiCo}_{0.8}\text{Mg}_{0.1}\text{O}_2$
比較電池Y2	$\text{LiMn}_{1.95}\text{Al}_{0.05}\text{O}_4$
比較電池Y3	$\text{LiMn}_2\text{O}_4$
比較電池Y4	$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$
比較電池Y5	$\text{LiCo}_{0.8}\text{Mg}_{0.1}\text{O}_2$
比較電池Y6	$\text{LiMn}_2\text{O}_4$ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$
比較電池Y7	$\text{LiMn}_{1.95}\text{Al}_{0.05}\text{O}_4$ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$
比較電池Y8	$\text{LiMn}_2\text{O}_4$ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{Mn}_{0.1}\text{O}_2$ $\text{LiCo}_{0.8}\text{Mg}_{0.1}\text{O}_2$
比較電池Y9	$\text{LiMn}_{1.95}\text{Al}_{0.05}\text{O}_4$ $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ $\text{LiCo}_{0.8}\text{Mg}_{0.1}\text{O}_2$

[0079] (Charge and discharge test) The charge and discharge test as well as the above-mentioned experiment 1 was performed in this invention cell D produced as mentioned above and A list about each cell of the comparison cells Y1-Y9, and it asked for 1C capacity maintenance factor and the 0.2C capacity maintenance factor. This result is shown in drawing 4.

[0080] By making a different-species element (aluminum) dissolve from contrast of the comparison cell Y2 and the comparison cell Y3 to the lithium-manganese multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) which is the first oxide shows that 1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved. This is because the crystal structure was strengthened and degradation of the crystal structure accompanying charge and discharge was controlled by making a different-species element dissolve to

the first oxide.

[0081] Moreover, it sets to a positive electrode from contrast with the comparison cell Y2 - the comparison cell Y4, and the comparison cell Y6 and the comparison cell Y7, and is  $\text{LiMn}_2\text{O}_4$ .  $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$  Moreover,  $\text{LiMn}_{1.95}\text{aluminum}_{0.05}\text{O}_4$   $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  By mixing shows that 1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved rather than the case where it is independent respectively. the mixture accompanying [ when this mixes a lithium-manganese system multiple oxide and a lithium-nickel-cobalt system multiple oxide ] charge and discharge -- it is because the whole expansion contraction was controlled.

[0082] Moreover, contrast with this invention cell A and the comparison cells Y6 and Y7 to  $\text{LiMn}_{1.95}\text{aluminum}_{0.05}\text{O}_4$   $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$  1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved greatly, and the difference of 1C capacity maintenance factor and a 0.2C capacity maintenance factor decreases greatly, and by mixing shows that the fall of the load characteristic accompanying a cycle can be controlled. Since the electronic state of the active material which consists of the second oxide changed for a start and the whole electronic conduction nature improved by making a different-species element dissolve to a lithium-manganese system multiple oxide and each lithium-nickel-cobalt system multiple oxide, and since the expansion contraction behavior accompanying those charges and discharges changed and contact of the particle comrade of the first oxide accompanying the progress which is a cycle, and the second oxide was maintained by stability, this is considered.

[0083] Moreover,  $\text{LiMn}_{1.95}\text{aluminum}_{0.05}\text{O}_4$  which is the first oxide in the positive electrode from contrast of the comparison cell Y1 and the comparison cells Y2 and Y5 By mixing  $\text{LiCo}_{0.9}\text{Mg}_{0.1}\text{O}_2$  which is the third oxide shows that 1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved rather than the case where it is independent respectively. The electronic conduction nature of the third oxide is higher than the first oxide, and the electronic state of the whole active material changes with mixing, and since electronic conduction nature improved further, this is considered.

[0084] Moreover, it sets to a positive electrode from contrast of the comparison cells Y6 and Y7 and the comparison cells Y8 and Y9.  $\text{LiMn}_2\text{O}_4$   $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$  Mixture,  $\text{LiMn}_{1.95}\text{aluminum}_{0.05}\text{O}_4$   $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  It is  $\text{LiCo}_{0.9}\text{Mg}_{0.1}\text{O}_2$  further to mixture. By mixing 1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved greatly, and the difference of 1C capacity maintenance factor and a 0.2C capacity maintenance factor decreases greatly, and it turns out that the fall of the load characteristic accompanying a cycle can be controlled. It is thought that this is also depended on the same reason as the above.

[0085] Furthermore, it sets to a positive electrode from contrast of this invention cell D and the comparison cells Y8 and Y9.  $\text{LiMn}_{1.95}\text{aluminum}_{0.05}\text{O}_4$   $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$   $\text{LiCo}_{0.9}\text{Mg}_{0.1}\text{O}_2$  1C capacity maintenance factor and a 0.2C capacity maintenance factor are improved by mixing. Moreover, the difference of 1C capacity maintenance factor and a 0.2C capacity maintenance factor decreases greatly, and it turns out that the fall of the load characteristic accompanying a cycle can be controlled. For a start whose electronic conduction nature improved, since the whole electronic state changed to the active material which consists of mixture of the second oxide further when electronic conduction nature mixed the third high oxide, this is considered.

[0086] It is empirical formula  $\text{LiMn}_{1.95}\text{aluminum}_{0.05}\text{O}_4$  as the first oxide which made the different-species element dissolve in the above-mentioned example. Although the oxide was used empirical formula  $\text{LiXMn}_{2-y}\text{M}_1\text{yO}_{4+z}$  ( $\text{M}_1$  -- aluminum, Co, and nickel --) When the lithium-manganese system multiple oxide which are at least one sort of elements chosen from the group which consists of Mg and Fe, and is expressed with  $0 \leq x \leq 1.2$ ,  $0 < y \leq 0.1$ , and  $-0.2 \leq z \leq 0.2$  is used, it is checking that the same effectiveness is acquired.

[0087] Moreover, although the thing of empirical formula  $\text{LiNi}_{0.6}\text{Co}_{0.3}\text{Mn}_{0.1}\text{O}_2$  was used in the above-mentioned example on the other hand as a lithium-nickel-cobalt system multiple oxide (the second oxide) which made the different-species element dissolve  $\text{LiM}_2\text{b NicCo}_d\text{O}_2$  ( $\text{M}_2$  is at least one sort of elements chosen from the group which consists of aluminum, Mn, Mg, and Ti) And when the

lithium-nickel-cobalt system multiple oxide expressed with  $0 < a < 1.3$ ,  $0.02 \leq b \leq 0.3$ ,  $0.02 \leq d/(c+d) \leq 0.9$ , and  $b+c+d=1$  is used, it is checking that the same effectiveness is acquired.

[0088] Moreover, on the other hand at the above-mentioned example, it is empirical formula  $\text{LiCo}_0.9\text{Mg}_{0.1}\text{O}_2$  as a lithium-cobalt system multiple oxide (the third oxide). Although the thing was used  $\text{LiM}_3\text{fCo}_1\text{-fO}_2$  ( $\text{M}_3$  is at least one sort of elements chosen from the group which consists of aluminum, Mn, Mg, and Ti) And when  $0 < e < 1.3$  and the lithium-cobalt system multiple oxide expressed with  $0 \leq f \leq 0.4$  are used, it is checking that the same effectiveness is acquired.

[0089] <Experiment 5> In this experiment 5, the content ratio of the first oxide in a positive-electrode ingredient was changed, and the property of a cell was compared.

[0090] this invention cell D of an example -- setting -- the weight of the first oxide, the second oxide, and the third oxide -- cells E1-E4 were produced like the example except changing a mixing ratio with 10:45:45, 20:40:40, 80:10:10, and 90:5:5. And 1C capacity maintenance factor and the 0.2C capacity maintenance factor were measured like the case of the above-mentioned experiment 1. The result is shown in drawing 5.

[0091] In this drawing 5, the result of the cell D (weight of the second oxide: weight : weight [ of the third oxide ] = of the first oxide 50:25:25) used in the above-mentioned experiment 4 is also written together. The result of drawing 5 R> 5 shows that 1C capacity maintenance factor and a 0.2C capacity maintenance factor improve, and the fall of the load characteristic accompanying a cycle can be controlled, when the mixing ratio of the lithium-manganese system multiple oxide in the above-mentioned mixture, i.e., the first oxide, is 20 - 80 % of the weight. This is considered to be because for contact of the particle comrade of the first oxide accompanying progress of a cycle and the lithium-nickel-cobalt system multiple oxide which is the second oxide to have been more maintainable to stability when the mixing ratio of the first oxide is in the above-mentioned range.

[0092] <Experiment 6> In this experiment 6, the content ratio of the second oxide and the third oxide in a positive-electrode ingredient was changed, and the property of a cell was compared.

[0093] this invention cell D of an example -- setting -- the weight of the first oxide, the second oxide, and the third oxide -- cells F1-F4 were produced like the example except changing a mixing ratio with 50:3:47, 50:5:45, 50:45:5, and 50:47:3. And 1C capacity maintenance factor and the 0.2C capacity maintenance factor were measured like the case of the above-mentioned experiment 1. The result is shown in drawing 6.

[0094] In this drawing 6, the result of the cell D (weight of the second oxide: weight : weight [ of the third oxide ] = of the first oxide 50:25:25) used in the above-mentioned experiment 4 is also written together. The result of drawing 6 R> 6 shows that 1C capacity maintenance factor and a 0.2C capacity maintenance factor improve, and the fall of the load characteristic accompanying a cycle can be controlled, when mixing ratios, the lithium-nickel-cobalt system multiple oxide in the above-mentioned mixture, i.e., the second oxide, and the lithium-cobalt system multiple oxide, i.e., third oxide, are 90:10-10:90 in a weight ratio. For a start whose electronic conduction nature improved, since the whole electronic state changed to the active material which consists of mixture of the second oxide further when electronic conduction nature mixed the third high oxide, this is considered.

[0095] <Experiment 7> In this experiment 7, the mean particle diameter of the third oxide in a positive-electrode ingredient was changed, and the property of a cell was compared.

[0096] In the above-mentioned this invention cell D, cells G1-G4 were produced like the above-mentioned example by controlling the grinding process at the time of compounding the third oxide except obtaining the active material which has the particle size shown in Table 4.

[0097]

[Table 4]



	第一酸化物の粒径	第二酸化物の粒径	第三酸化物の粒径
電池 G 1	1 5 $\mu$ m	1 0 $\mu$ m	2 $\mu$ m
電池 G 2	1 5 $\mu$ m	1 0 $\mu$ m	3 $\mu$ m
電池 D	1 5 $\mu$ m	1 0 $\mu$ m	1 0 $\mu$ m
電池 G 3	1 5 $\mu$ m	1 0 $\mu$ m	1 5 $\mu$ m
電池 G 4	1 5 $\mu$ m	1 0 $\mu$ m	2 0 $\mu$ m

[0098] And 1C capacity maintenance factor and the 0.2C capacity maintenance factor were measured like the case of the above-mentioned experiment 1 using the above-mentioned cells G1-G4. The result is shown in drawing 7. The data of this invention cell D prepared for this drawing 7 in the experiment 4 mentioned above are also shown collectively.

[0099] When the mean particle diameter of the third oxide which is a lithium-cobalt system multiple oxide is in the range which is 3-15 micrometers from the result of drawing 7, it turns out that 1C capacity maintenance factor and a 0.2C capacity maintenance factor improve, and the fall of the load characteristic accompanying a cycle can be controlled especially.

[0100] the case where the mean particle diameter of the third oxide is especially contained in the above-mentioned range -- contact of the particle comrade of each multiple oxide -- more -- increasing -- a mixture -- since the whole electronic state changes and electronic conduction nature improves, and since expansion contraction of each multiple oxide is offset more effectively, the property of Cells G2 and D and G3 is considered to be good.

[0101]

[Effect of the Invention] As explained in full detail above, according to this invention, the fall of the load characteristic accompanying a cycle can offer fewer lithium secondary batteries.

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[Translation done.]